Supplementary Information

Cu(II) nanocluster-grafted, Nb-doped TiO_2 as an efficient visible-light-sensitive photocatalysts based on energy-level matching between surface and bulk states

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Table S1. ICP measurement of Cu(II)-$Nb_xTi_{1-x}O_2$.

sample	Cu(II)-$Nb_xTi_{1-x}O_2$				
Initial Nb (wt%)	0.01	0.05	0.1	0.5	1
Measured Nb (wt%)	0.011	0.055	0.111	0.506	0.972

Table S2. BET surface area of bare TiO_2, $Nb_xTi_{1-x}O_2$, Cu(II)-TiO_2, and Cu(II)-$Nb_xTi_{1-x}O_2$.

Sample	TiO_2	$Nb_xTi_{1-x}O_2$	Cu(II)-TiO_2	Cu(II)-$Nb_xTi_{1-x}O_2$
BET surface area (m^2/g)	6.03	5.76	5.93	5.84

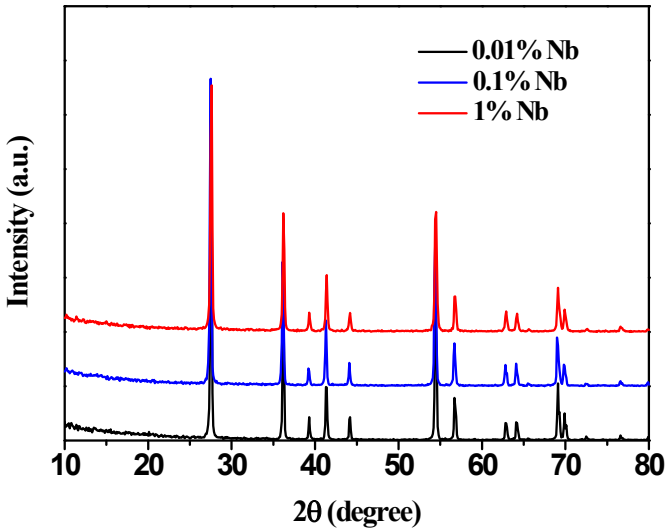

Figure S1. XRD patterns of 0.01 wt%, 0.1 wt% and 1 wt% Nb doped TiO_2.

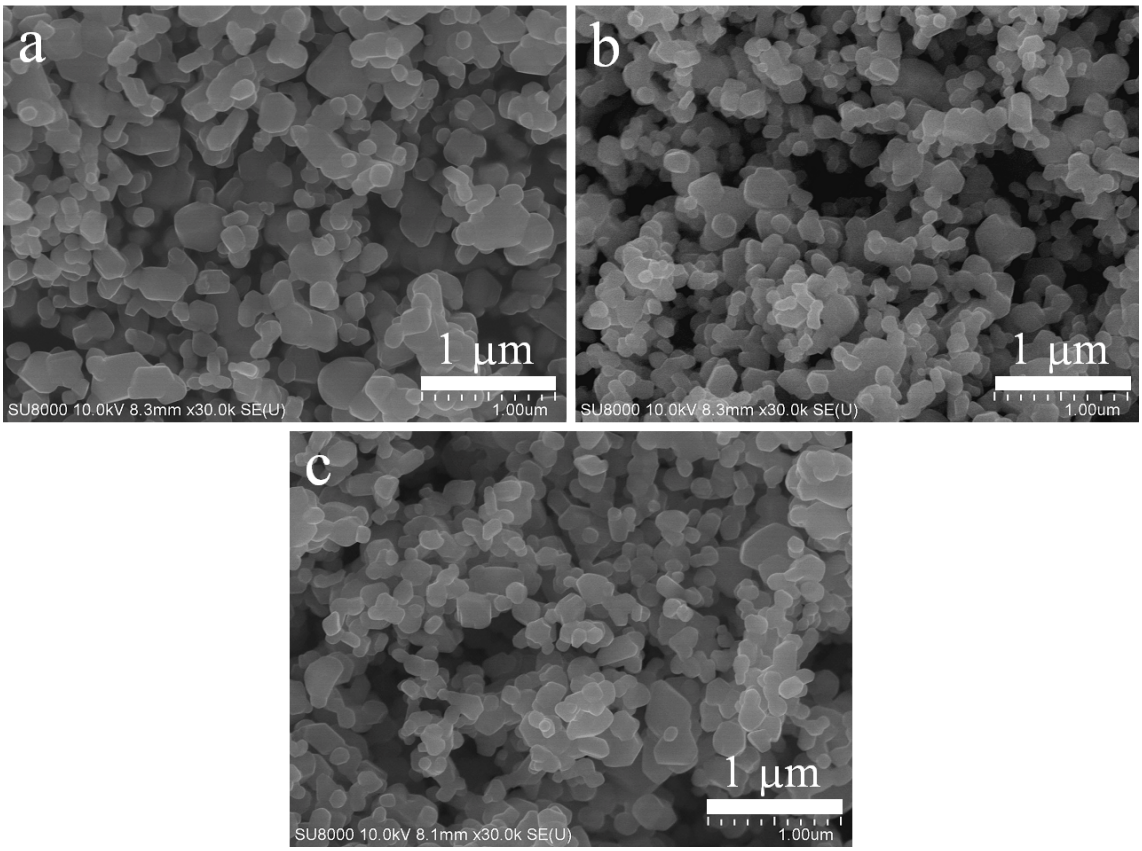

Figure S2. SEM images of $Nb_xTi_{1-x}O_2$ at (a) x=0.01 wt%, (b) x=0.1 wt%, and (c) x=1 wt%, respectively.

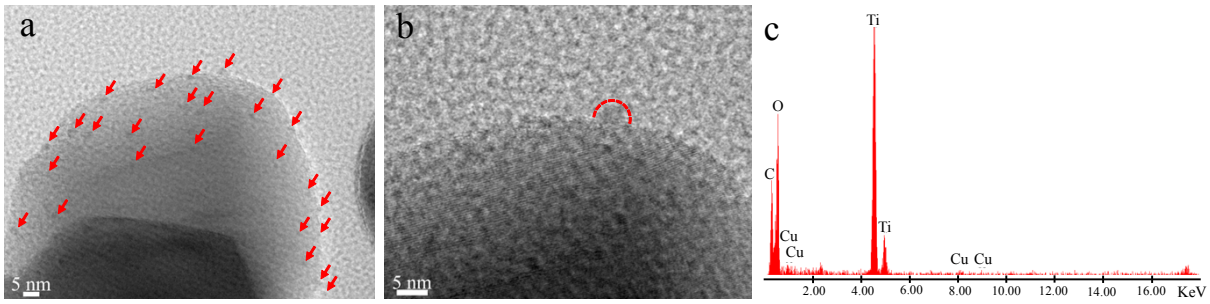

Figure S3. (a) TEM, (b) HRTEM images and (c) EDS pattern of Cu(II)-$Nb_xTi_{1-x}O_2$. Nanoclusters (marked by red arrows) were highly dispersed on the $Nb_xTi_{1-x}O_2$ surface. In Figure S3b, a short dashed curve is outlined the Cu(II) nanoclusters. The good attachment of nanoclusters and $Nb_xTi_{1-x}O_2$ was clearly observed. Figure S3c shows the result of EDS point analysis on the corresponding Cu(II) nanocluster marked by the short dashed curve in Figure S3b.

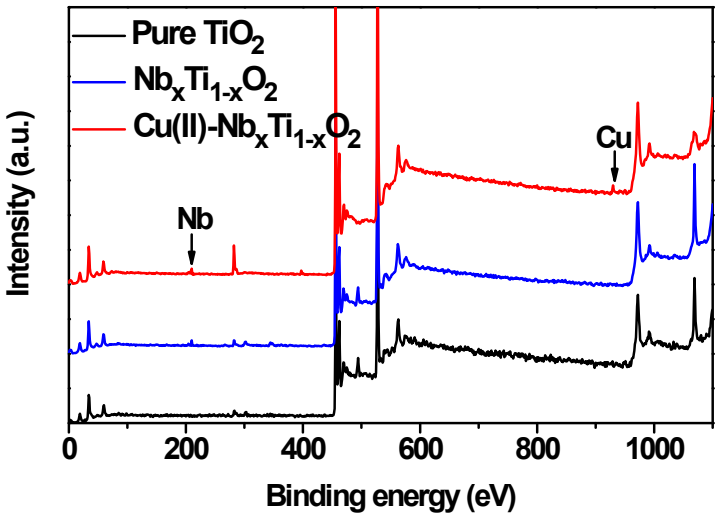

Figure S4. Full-scale XPS spectra of pure TiO_2, $Nb_xTi_{1-x}O_2$, and Cu(II)-$Nb_xTi_{1-x}O_2$, respectively.

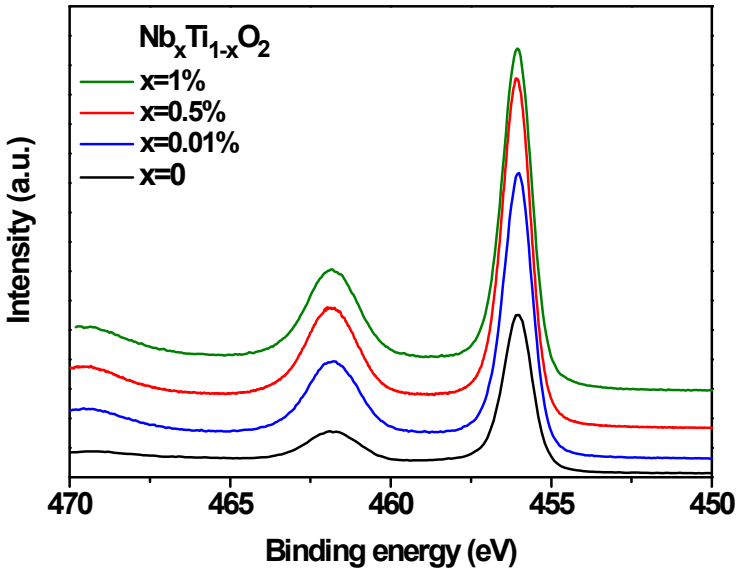

Figure S5. Ti 2p core-level spectra of pure TiO_2, and $Nb_xTi_{1-x}O_2$ at x= 0.01 wt%, 0.5 wt% and 1 wt%, respectively.

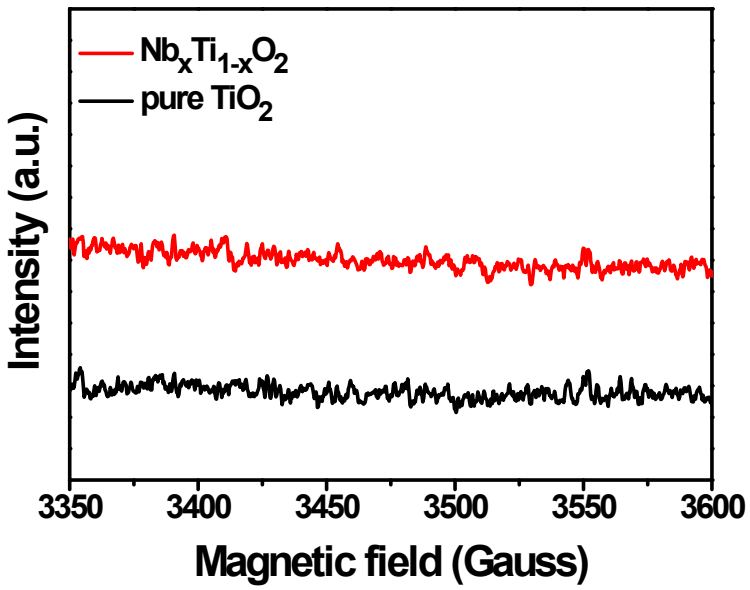

Figure S6. ESR spectra of pure TiO_2 and $Nb_xTi_{1-x}O_2$ at 0.1 wt%.

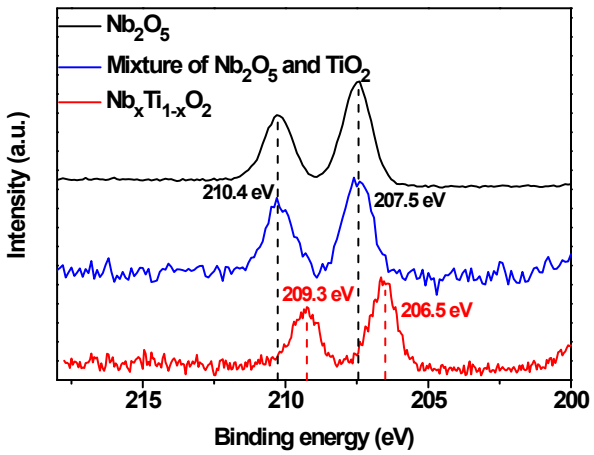

Figure S7. Nb 3d core-level spectra of pure Nb_2O_5, physical mixed Nb_2O_5 and TiO_2 and $Nb_xTi_{1-x}O_2$ at x= 0.1 wt%, respectively.

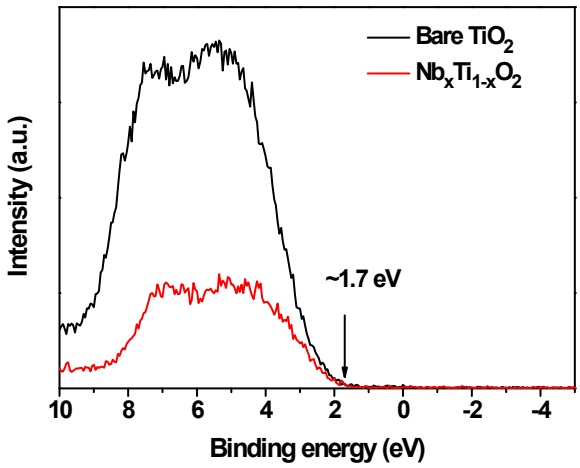

Figure S8. VB XPS of bare TiO_2, and $Nb_xTi_{1-x}O_2$ at x= 0.1 wt%, respectively.

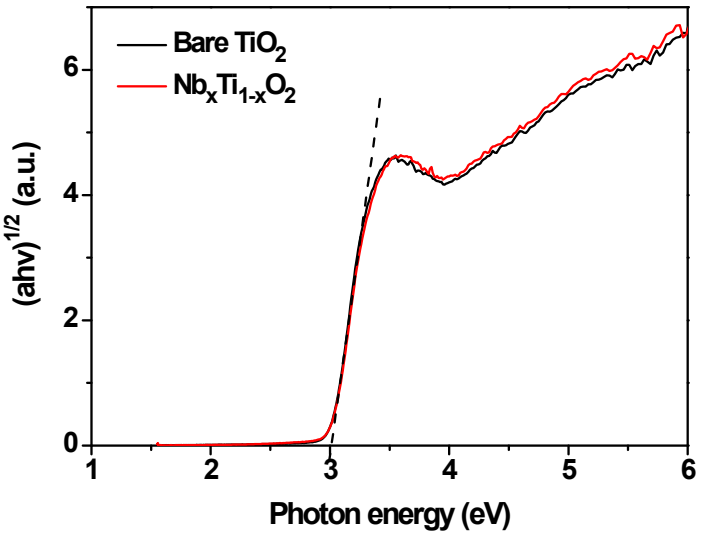

Figure S9, Band gap of bare TiO_2 and $Nb_xTi_{1-x}O_2$ according to the Kubelka−Munk function.

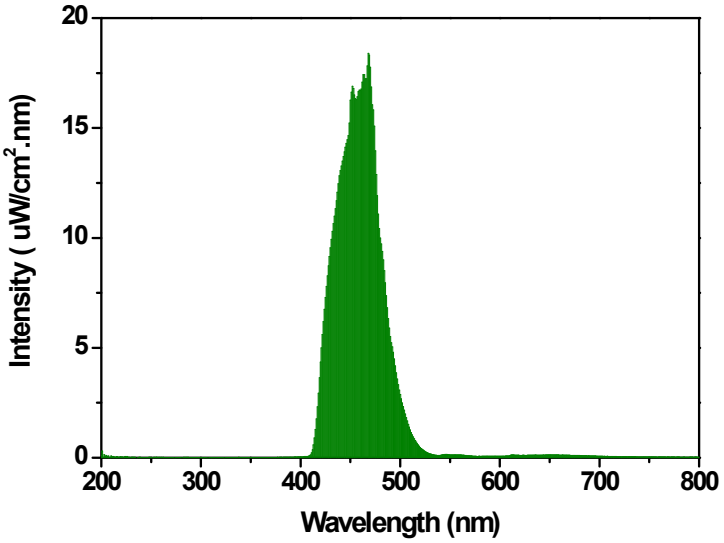

Figure S10. The light source for the visible light irradiation.

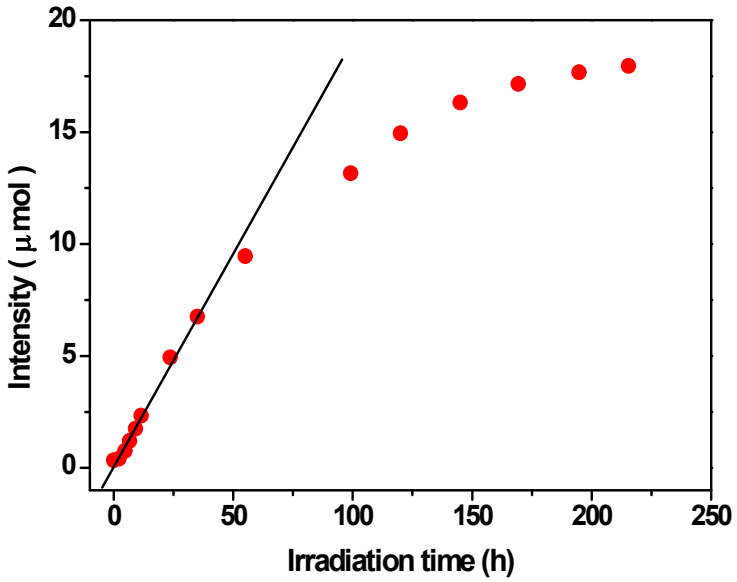

Figure S11. The CO_2 generation curve over Cu(II)-$Nb_xTi_{1-x}O_2$ (x=0.1 wt%) sample under visible light irradiation. The CO_2 generation rate (R_{CO2}) was obtained from the slope of the CO_2 generation curve between the irradiation time of ca. 0 to 30 h.

The calculation of quantum efficiency (QE) was conducted using the same procedure reported in literature (*1*).

Take Cu(II)-$Nb_xTi_{1-x}O_2$ at x=0.1% sample for example. Under the visible light irradiation, the wavelength of visible light is from 400 to 530 nm, and the light intensity is 1 mW/cm^2. The irradiating area is 5.5 cm^2. Therefore, the absorption rate of incident photons (R^a_p) was determined to be 7.91×10^{14} quanta·sec^{-1} using the following equation: $R^a_p=\int_{400}^{530} S\times\alpha\times I$ (S is the area of the sample, α is the light absorption and I is the light intensity at each wavelength). As for CO_2 generation, assuming that the reaction from IPA to CO_2 is proceeded: $C_3H_8O+5H_2O+18h^+\rightarrow3CO_2+18H^+$, that is, six photons are required to produce one CO_2 molecule. The CO_2 generation rate (R_{CO2}) was obtained from the slope of the CO_2 generation curve in Figure S9. As shown in Figure S9, R_{CO2} was determined to be 0.20 μmol·h^{-1}. Thus the QE for CO_2 generations were

calculated using the following equation:

QE = 6×CO_2 generation rate/absorption rate of incident photon

=6×(2.0×10^{-1}×10^{-6}/3.6×10^{3})mol·sec-1×6.0×10^{23}quanta·mol-

^{1}/7.91×10^{14}quanta·sec^{-1}

= 25.3×10^{-1} (25.3%).

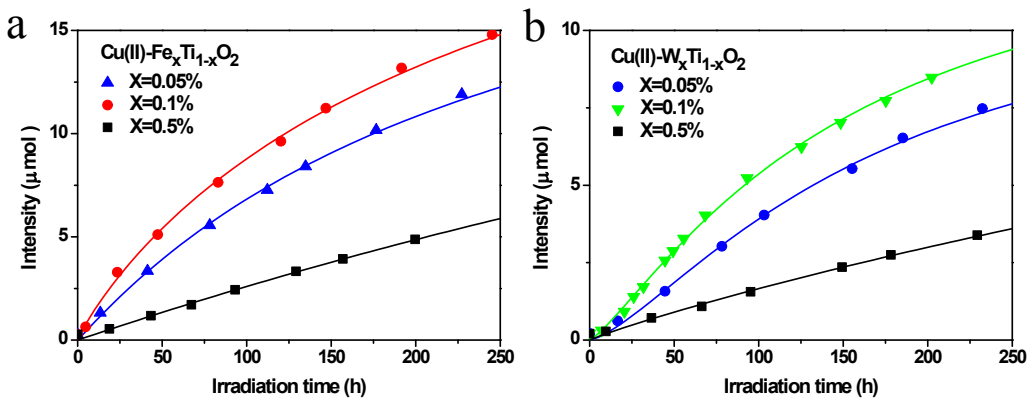

Figure S12. CO_2 generation over (a) Cu(II)-$Fe_xTi_{1-x}O_2$ at x=0.05 wt%, 0.1 wt%, and 0.5 wt%, and (b) Cu(II)-$W_xTi_{1-x}O_2$ at x=0.05 wt%, 0.1 wt%, and 0.5 wt%, under visible light irradiation.

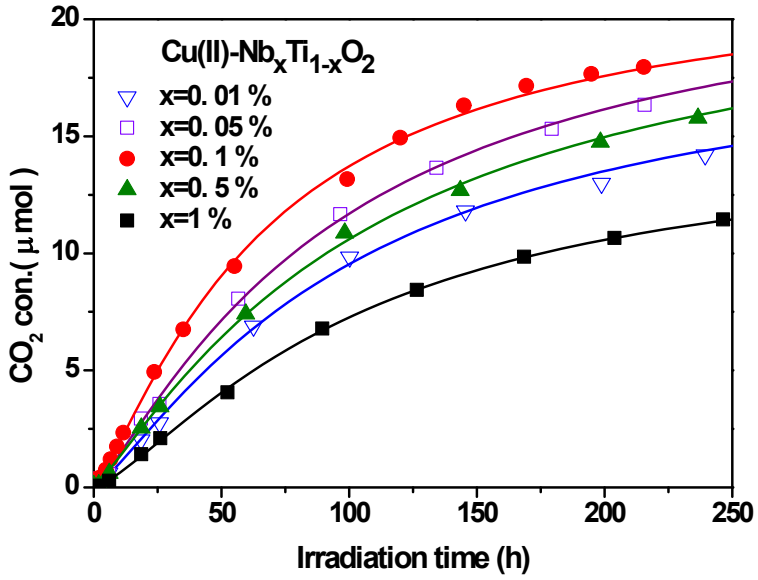

Figure S13. CO_2 generation over Cu(II)-$Nb_xTi_{1-x}O_2$ at x=0.01 wt%, 0.05 wt%, 0.1 wt%, 0.5 wt% and 0.5 wt% under visible light irradiation.

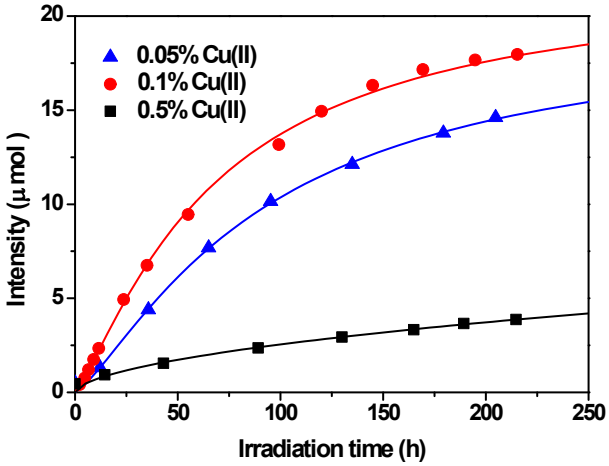

Figure S14. CO_2 generation over Cu(II)-$Nb_xTi_{1-x}O_2$ grafted with x=0.05 wt%, 0.1 wt%, and 0.5 wt% Cu(II) nanolcusters under visible light irradiation.

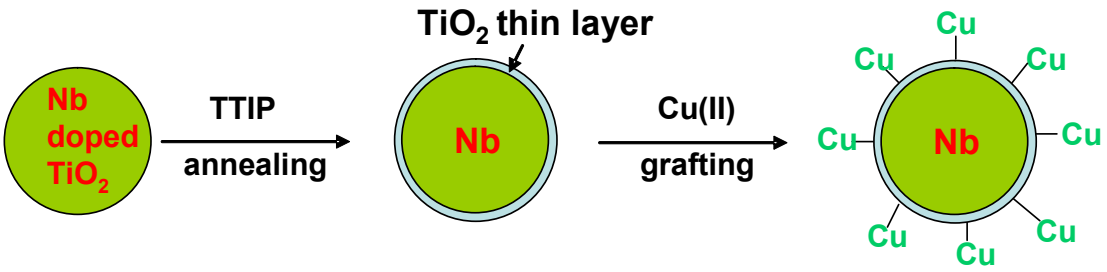

Figure S15. Scheme for the preparation of the samples by introducing a TiO_2 thin layer between Cu(II) nanoclusters and $Nb_xTi_{1-x}O_2$ (x=0.1 wt%).

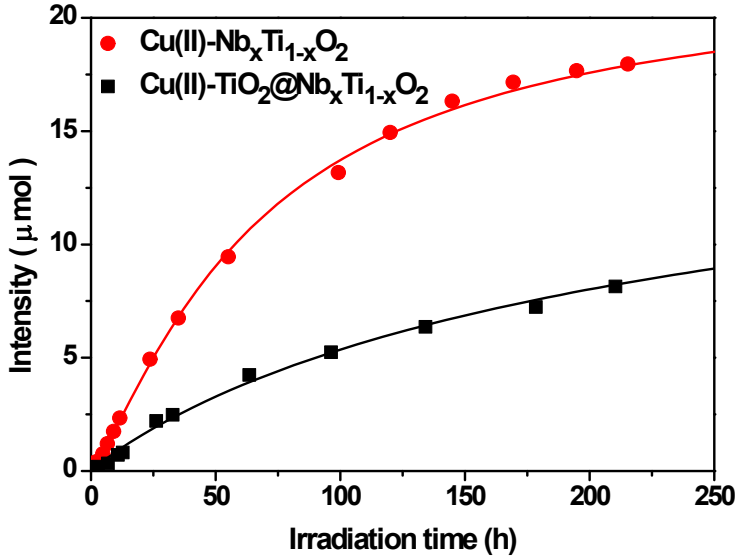

Figure S16. The CO_2 generation curve over Cu(II)-$Nb_xTi_{1-x}O_2$ and Cu(II)-TiO_2@$Nb_xTi_{1-x}O_2$ (x=0.1 wt%) samples under the same visible light irradiation.

References

1. H. G. Yu, H. Irie, Y. Shimodaira, Y. Hosogi, Y. Kuroda, M. Miyauchi, K. Hashimoto, *J. Phys. Chem. C* 2010, **114**, 16481-16487.